

# Effect of Cross Linked Chitosan Filler on Degradability Properties of Chitosan Bio-composites

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## Abstract

The degradability properties of cross linked chitosan (ODAC) filled chitosan bio-composites were investigated under swelling analysis. The swelling analysis was performed under the pH medium of 2 to 12, and recorded as swelling ratio (Qt) and swelling rate (Qr). The optimum Qt and Qr values of the bio-composites occurred at pH 7. The Qt and Qr values reduced linearly with the ODAC filler content up to 8 wt/v %. The Fourier Transform Infra-Red (FTIR) analysis of the bio-composites confirms a good compatibility, rigidity and homogenous of the Cs matrix and DPAC filler. This in turn increased the stability of the bio-composites as visualized by FTIR analysis of swollen sample.

## Keywords

Biopolymers; Composites; Cross linking; Compatibility; Degradability

## Introduction

Chitosan (Cs) has received much attention in recent years due to its bio-degradability, non-toxicity and bio-compatibility properties. Cs is one of the polysaccharides derived from chitin; a bio-polymer originated from crustacean shells. It has many possible uses in biomaterials, waste water treatment, agriculture, packaging, food supplements and other fields and has also investigated as potential engineering materials. However, it has been found to be degraded under most of conditions. Due to the abundant with polar groups with the semi crystalline nature, allows Cs to absorb the moisture from surrounding. Hua et al. (2010) has pointed out the hydrophilicity has a strong effect on chain mobility of Cs polymer. The hydrophilic properties provided the Cs with loose polymer networks, extra voids and porous structure.

One way to reduce the degradability is chemically modifying the Cs structure and there has been extensive research regarding the modification. Liu et al. (2005), using linoleic acid had successfully reduced the hydrophilicity and enzymatic degradation of Cs film. The hydrophilicity of Cs was also reduced by grafting the Cs polymer with hydrophobization agent. However, in the majority of cases, the modification is normally involved high production cost and reduced the mechanical properties of the Cs.

Therefore, there was a rational to reinforce the Cs with rigid filler and produce Cs bio-composites. Numerous experiments have established addition of the filler causes a more stable, resist, durable of Cs with reasonable production cost. The bio-composites also demonstrate in the reduction on adsorption and swelling properties of Cs. For example, the swelling properties are more controllable for the Cs with titanium oxide bio-composites as compared to the neat Cs film. Early data demonstrated addition of 28 wt% of kenaf dust reduced almost 45% on swelling ratio of Cs bio-composites. However, the basic issue of bio-composites is, the properties are very much dependent on state of the mix, compatibility of bio-composite components and rigidity of the filler. Even though large numbers of studies on Cs bio-composites with respect to different type of filler (organic or inorganic) were done; only limited study proved the compatibility and rigidity of the combination. The mechanical bonding such as interlock, cohesion adhesion and stacking while, physical bonding such as polar-polar interaction, Van de Waals, polarization, dipole-dipole interactions and hydrogen bonding, are insignificantly reduced the hydrophilic nature of the

Cs film. Regardless the types of filler and matrix, these types of interactions limit the compatibility and homogeneity between the bio-composites' components.

Within this line, it is rational of derived the rigid filler from the similar sources of the Cs film. A cross linked Cs (XCs) filler is composed of a linear Cs polymer anchored by the cross linking agents. The rigidity of the filler brought from its cross linking structure. The similarity in the polymer back bones of filler and matrix results in the more compatible interfacial region of the bio-composites.

### Materials and Methodology

Cs powder (DD=78 ;  $M_w = 125\,000\text{ g mol}^{-1}$ ) was purchased from Hunza Pharmaceutical (M) Sdn Bhd. Acetic acid (AcOH), chloroform, methanol, N-methyl pyrrolidone (NMP), sodium hydroxide (NaOH) and pH buffer solution (Phosphate and Acetate buffer solution; the pH values were checked precisely by a pH meter) were purchased from Merck (Co) Germany. Doubly distilled de-ionized water was used.

### Preparation of the ODAC Filler

The ODAC filler was synthesized with accordance to the previous reports. Fig.1 illustrated the chemical structure of the ODAC filler.

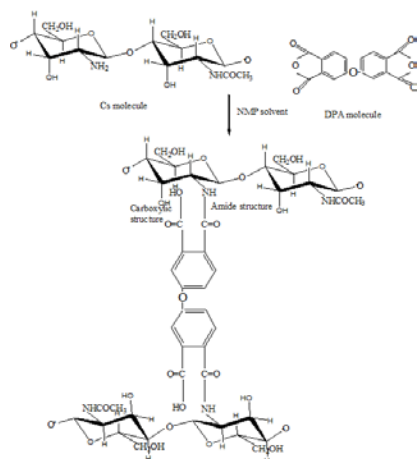


FIG. 1 THE CHEMICAL STRUCTURE OF ODAC FILLER

### Preparation of the bio-composites

The bio-composites were prepared with accordance to the previous reports. Each of bio-composites was abbreviated as X-ODAC (where X gives the wt/v% of the ODAC filler)

### Thickness measurements of the bio-composites

Thickness of bio-composites was measured with hand-

held digital micrometer (Mitutoyo, Japan) having a sensitivity of 0.0001 mm.

### Swelling analysis of the bio-composites

The bio-composites were immersed in buffer solutions with difference pH values (pH 2 to 12) at 30°C. The swollen bio-composites were removed at certain intervals and directly weighted. The procedure was repeated until there was no further increase in weight. The swelling ratio ( $Q_t$ ) was calculated by the weight of the swollen bio-composites at a specific time ( $t$ ) divided by the initial weight in the dry state. Meanwhile, the swelling rate ( $Q_r$ ) was determined by the slope of the  $Q_t$  over  $t$ .

### FTIR characterization of the bio-composites

FTIR spectra bio-composites were recorded by the attenuated total reflection method (ATR) using Fourier Transform Infrared [Model: FTIR Spectrum One, Perkin Elmer]. The spectra was recorded over a range of 4000 to 400  $\text{cm}^{-1}$  with resolution of 2  $\text{cm}^{-1}$  and averaged over 10 times of scanning.

## Results and Discussion

### Inter molecules interactions of the bio-composites

The compatibility in bio-composites is demonstrated by the formation of electrostatic interactions and inter/intra H bonds between the Cs matrix and ODAC filler (Fig 2a and b). As the content of Cs matrix was fixed, both of interactions are the function of the ODAC filler.

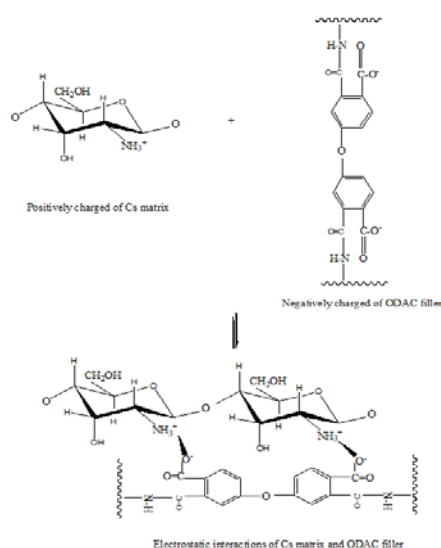


FIG. 2 a ELECTROSTATIC INTERACTION OF  $\text{NH}_2$  GROUPS (CS MOLECULES) AND  $\text{COOH}$  GROUPS (ODAC MOLECULES)

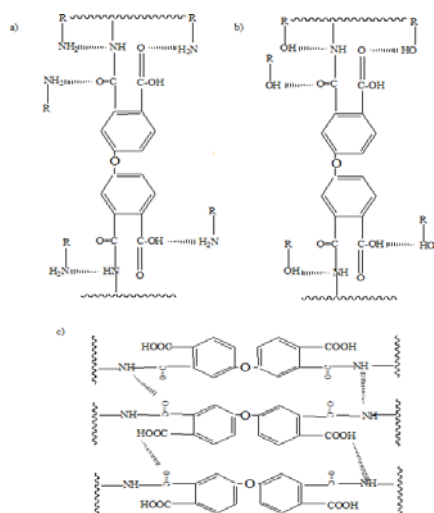


FIG. 2 b INTER HYDROGEN BONDS OF (A)  $\text{NH}_2$  GROUPS (CS MOLECULES) AND POLAR GROUPS (ODAC MOLECULES), (B)  $\text{OH}$  GROUPS (CS MOLECULES) AND POLAR GROUPS (ODAC MOLECULES)

Electrostatic interactions between the Cs and ODAC molecules result from the ionization state of the  $\text{NH}_2$  groups of Cs molecules and  $\text{COOH}$  groups of the ODAC molecules (Fig. 2a). The  $\text{NH}_2$  groups in the Cs molecules become positively charged after the protonization with  $\text{H}^+$  ions:  $\text{NH}_2 + \text{H}^+ \leftrightarrow \text{NH}_3^+$ . The ODAC molecules become negatively charged due to the dissociation of  $\text{COOH}$  groups with  $\text{H}_2\text{O}$  molecules:  $\text{COOH} \leftrightarrow \text{COO}^- + \text{H}^+$ . Then  $\text{NH}_3^+$  cations subsequently interacted with the  $\text{COO}^-$  anions to form the electrostatic interactions.

The inter/intra H bonds occurred within the polar groups of the bio-composites;  $\text{OH}$ ,  $\text{NH}_2$ ,  $\text{COOH}$ ,  $\text{OH}$ ,  $\text{NH-R}$  and  $\text{C-N}$  (Fig. 2b). At the ODAC filler content of 0 to 2 wt/v %, the inter H bonds are predominantly occurred within the Cs matrix (Fig. 2b(i)). At the filler content of 4 to 8 wt/v %, the interaction occurred within the Cs matrix and the ODAC filler (Fig. 2b(ii)). The interactions are significantly changed from inter to intra molecular, as the content of the ODAC filler reached to 12 wt/v % (Fig. 2b(iii)).

### Thickness of the bio-composites

The thickness of the bio-composites increased from 15.4 to 28.5 % with the addition of 2 to 8 wt/v % ODAC filler, respectively (Fig. 3). At this filler content, the ODAC filler is entrapped homogeneously with Cs matrix, results in smooth with mostly constant in thickness values of the bio-composites. The thickness values are significantly increased 14.3 % with the addition of 10 to 12 wt/v % ODAC filler, and demonstrated inconsistency reading.

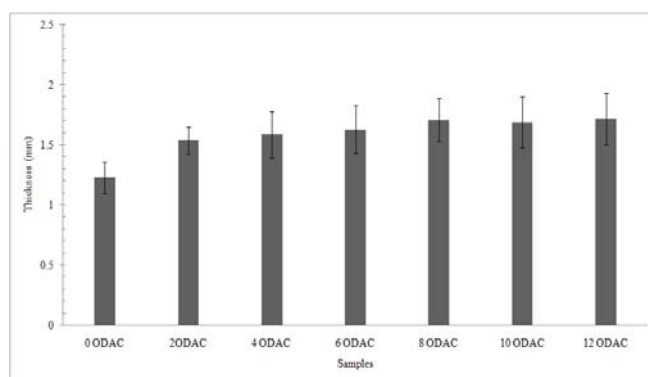


FIG. 3 THICKNESS VALUES OF THE BIO-COMPOSITES

### Swelling properties of the bio-composites

#### Swelling in acidic media (pH 2 to 6)

The swelling profile of the bio-composites in difference pH acidic medium (pH 2 to 6) is illustrated in Fig. 4 and Fig. 5. Generally, a good correlation is observed between the swelling ratio ( $Q_t$ ), equilibrium time ( $t$ ) and swelling rate ( $Q_r$ ) with the content of ODAC filler (Fig. 5a and b). The  $Q_t$ ,  $Q_r$  and  $t$  values are systematically increased and the swelling mechanism is favorable with the reduction of ODAC filler. The result is consistent with the bio-composites of 2 to 8 wt/v % of ODAC filler. Meanwhile, the  $Q_t$ ,  $Q_r$  and  $t$  values of the bio-composites with 10 to 12 wt/v % of the ODAC filler are identically to neat Cs film.

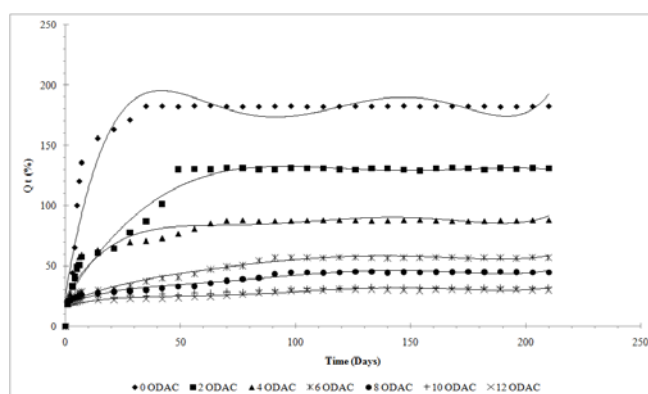


FIG. 4 a THE SWELLING PROFILE OF THE BIO-COMPOSITES IN SWOLLEN MEDIA OF PH 2

It found that the swelling profile of the bio-composites is influenced by the number of free  $\text{NH}_2$  groups in Cs matrix. The number of groups reduces with the addition of ODAC filler. The reduction is brought by the formation of electrostatic interactions and inters H bonds. Generally, the  $\text{NH}_2$  groups provided an active site for the protonization of Cs in the acidic media.

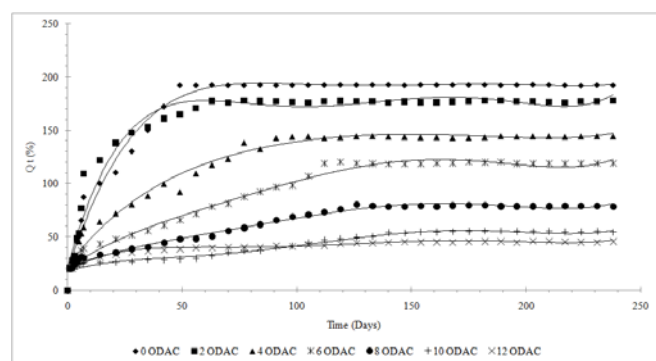


FIG. 4 b THE SWELLING PROFILE OF THE BIO-COMPOSITES IN SWOLLEN MEDIA OF PH 4

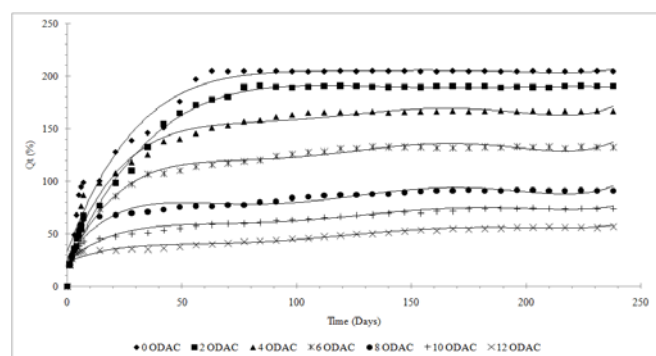


FIG. 4 c THE SWELLING PROFILE OF THE BIO-COMPOSITES IN SWOLLEN MEDIA OF PH 6

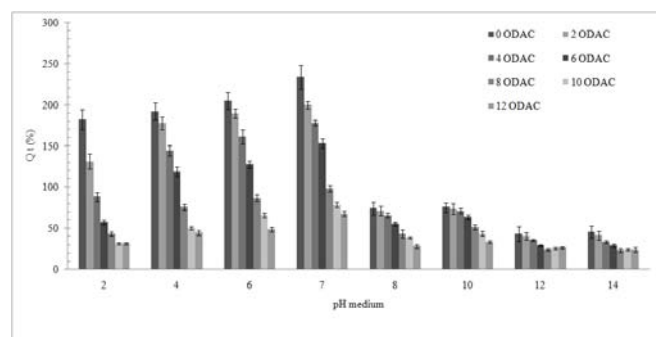


FIG. 5 a THE SUMMARIZED OF QT VALUES OF THE BIO-COMPOSITES IN DIFFERENT PH MEDIA

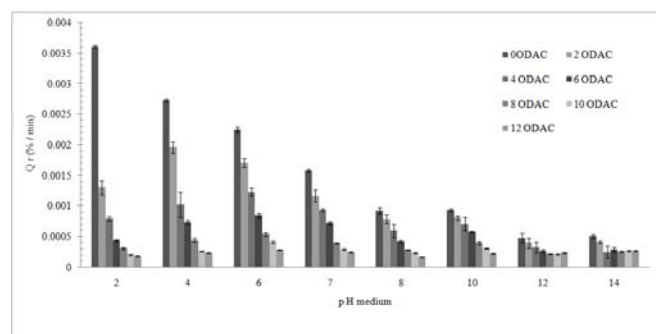


FIG. 5 b THE SUMMARIZED OF QR VALUES OF THE BIO-COMPOSITES IN DIFFERENT PH MEDIA

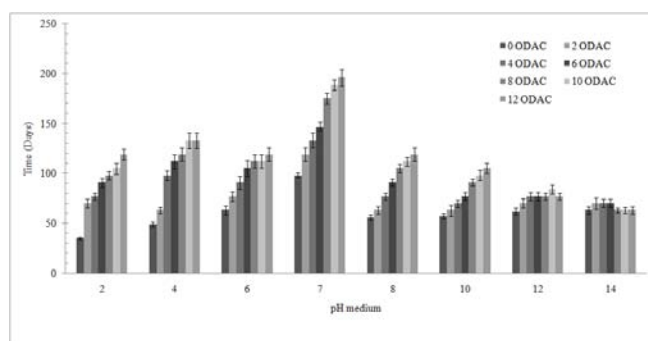


FIG. 5 c THE SUMMARIZED OF T VALUES OF THE BIO-COMPOSITES IN DIFFERENT PH MEDIA

Due to the protonization, the Cs polymer chains moved apart and swelling process is simultaneously introduced to the bio-composites. Additionally, the swelling profile influenced by the compact in the bio-composites structure. The bio-composites structure becomes compressed, less flexibility and had a permanently network structure due to the cross linked structure of the ODAC filler. Thus, it is difficult for the liquid to migrate along the bio-composites and significantly reduced the swelling mechanism of the bio-composites. The swelling profile also related to the bulky structure of the benzene ring in ODAC molecules. During the swelling process, the benzene ring reduced the counter  $H^+$  ions of the bio-composites. The polar groups of ODAC filler tightly capped by the benzene ring; the assessment of  $H^+$  ions into the bio-composites are limited. The benzene ring also increased the molecular weight of the ODAC molecules per unit monomer and reduced the net adsorption ability of the bio-composites.

However, at the excess content of ODAC filler (10 to 12 wt/v %), the weak interfacial regions occurred and supplied the bio-composites with low strength properties. At this point, the swelling profile of the bio-composites is slightly reduced and results in lower  $Q_t$  values.

The equilibrium time ( $t$ ) of swollen bio-composites is increased with the content of ODAC filler (Fig. 5c). The  $t$  value is increased almost 166.7 and 266.7 % for the bio-composites with 2 to 4 wt/v% of ODAC filler. The increment indicates, the ODAC filler reduced the sorption properties of the bio-composites. The rigid structure of ODAC filler balanced between the adsorption of  $H^+$  ions and reinforcement of the bio-composites.

Fig. 4a, b and c indicate the effect of the pH media on swelling profile of the bio-composites. The swelling

profile is more significant in the greater concentration of  $H^+$  ions (at lower pH media). The  $Q_r$  and  $Q_t$  values of the bio-composites decreased as the pH media increased. Regardless on the content of the ODAC filler, the  $Q_t$  and  $Q_r$  values of the bio-composites are originated from swollen media of pH 2. Therefore, the concentration of  $H^+$  ions increased with the swelling properties of the bio-composites. The  $H^+$  ion changes in the charge density of the bio-composites via the protonization of Cs matrix and ionization of ODAC filler; it increased osmotic pressure of the bio-composites. The pressure reduces the surface stability of the bio-composites and leads to more adsorptions of  $H^+$  ions.

### Swelling in neutral media (pH 7)

Fig. 6 illustrated the swelling profile of the bio-composites in neutral media. The highest and lowest  $Q_t$  and  $Q_r$  values are recorded by the ODAC and 8ODAC bio-composites, respectively. The bio-composites with 0 to 4 wt/v % of ODAC filler exhibit higher values  $Q_t$  and  $Q_r$  values, with almost double than those with 6 to 8 wt/v % (Fig. 5a and b).

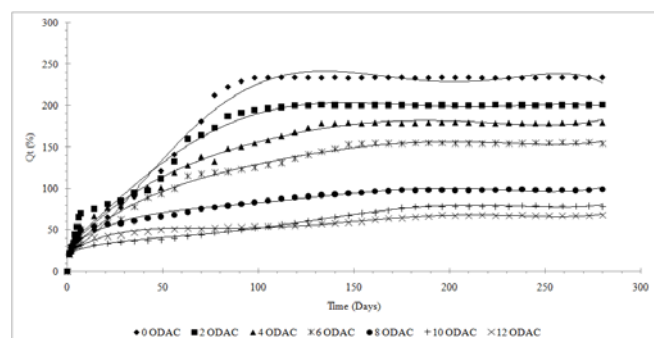


FIG. 6 THE SWELLING PROFILE OF THE BIO-COMPOSITES IN SWOLLEN MEDIA OF PH 7

Addition of the ODAC filler reduced the swelling mechanism of the bio-composites in neutral media. The electrostatic interaction and inter H bonds limit chain extensibility, and trapped the polar groups of the bio-composites. Additionally, the cross-linked, bulky and hydrophobic structure of the ODAC filler limits the ionic interactions and adsorption of  $H_2O$  molecules into the bio-composites. Furthermore, number of polar groups also responses to the swelling mechanism of the bio-composites. The main difference between the Cs and ODAC molecules consist in that the former contains  $NH_2$ ,  $OH$  and  $NH-R$ , while the latter contains only  $OH$  and  $NH-R$  groups. The  $NH_2$  groups are more accessible by  $H_2O$  molecules, rather than other polar groups. Thus, greater ODAC-

contained bio-composites had lower adsorption as well as swelling mechanism.

At 10 to 12 wt/v % of ODAC filler, the bio-composites polymer chains are restricted due to the excess content of the filler. The excess content supplied freer polar groups to the bio-composites. The ODAC filler tends to form self-inter-molecular interactions due to the excess content. The interactions induced in-homogenous structure of bio-composites and initiated a progressively adsorption and swelling process of the bio-composites. This, consequently, reduces the stability of the bio-composites during usage and storing.

### Swelling in alkaline media (pH 8 to 12)

Fig. 7 a, b and c reports the swelling profile of the bio-composites in alkaline media. The  $Q_t$  and  $t$  values of the bio-composites are relatively constant in all alkaline media (pH 8 to 12). The consistency is brought by the molecular structure of ODAC filler. The  $COOH$  groups of the ODAC filler tend to produce  $COO^-$  ions in more alkaline media [15; 18]. The  $COO^-$  ions become a host to shove the  $OH^-$  ions from the media. This results in balance on the ion concentration of alkaline media and the dimensional structure of the bio-composites. Furthermore, addition of ODAC filler induced more dense structure of the bio-composites. The osmotic pressure of bio-composites decreased and limits the diffusion of the swollen media [17; 21]. Additionally, in the alkaline media, the  $NH_2$  groups of Cs matrix become de-protonated.

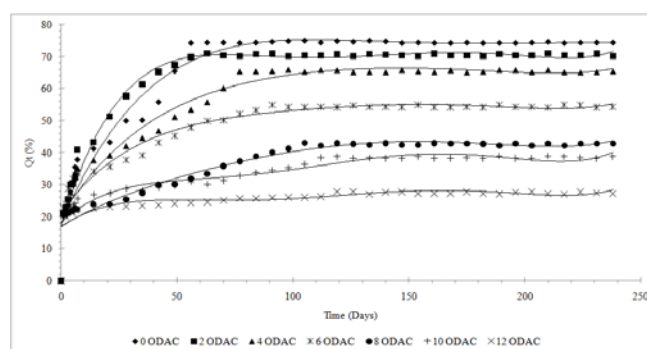


FIG. 7 a THE SWELLING PROFILE OF THE BIO-COMPOSITES IN SWOLLEN MEDIA OF PH 8

The de-protonization of Cs polymer allows the shrinkage rather than swelling process of the bio-composites [22]. Fig. 5a and b suggests that, the minimum  $Q_t$  and  $Q_r$  values is recorded for the 8ODAC bio-composites, with 0.008 and 62 %  $min^{-1}$ , respectively.



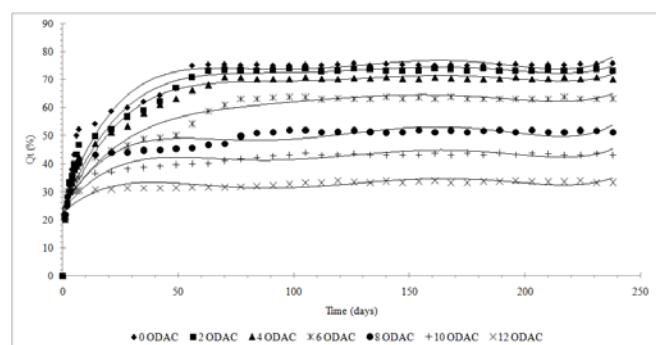


FIG. 7 b THE SWELLING PROFILE OF THE BIO-COMPOSITES IN SWOLLEN MEDIA OF PH 10

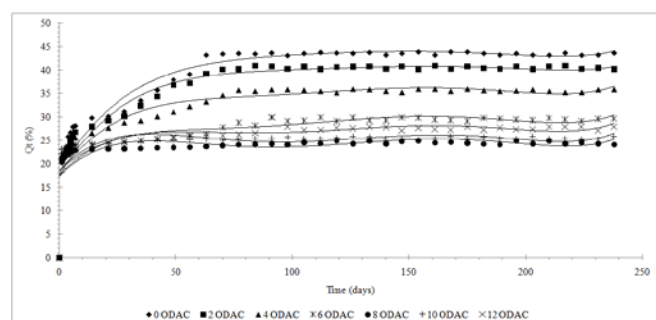


FIG. 7 c THE SWELLING PROFILE OF THE BIO-COMPOSITES IN SWOLLEN MEDIA OF PH 12

These values increased with the reduction of the ODAC filler and reached to the maximum for the unfilled bio-composites. The exact mechanisms are not understood, but it seems likely that; the thinner bio-composites exhibited more internal stresses in alkaline media. This consequently, increased the diffusion rates of OH<sup>-</sup> ions and swelling process of the bio-composites.

## FTIR analysis

### FTIR analysis of non swollen bio-composites

The FTIR spectrum of bio-composites is illustrated in Fig. 8. Generally, the molecular structure of Cs matrix is assigned as follows; 2929 and 2874 cm<sup>-1</sup> (aliphatic C-H stretching), 1385 cm<sup>-1</sup> (C-H stretching), 1651 cm<sup>-1</sup> (N-H bending), 1560 cm<sup>-1</sup> (N-H bending), 1425 and 1401 cm<sup>-1</sup> (C-H bending), 1155 cm<sup>-1</sup> (C-O stretching), 1138 and 1095 cm<sup>-1</sup> (C-O stretching), 1025 cm<sup>-1</sup> (OH deformation), 1151 and 898 cm<sup>-1</sup> (saccharine structure).

Addition of ODAC filler into Cs matrix markedly induced some alteration in the FTIR spectrum. The progressive reduction in the intensity peaks of 3440 cm<sup>-1</sup>, 2910 cm<sup>-1</sup>, 1417 cm<sup>-1</sup>, 1377 cm<sup>-1</sup> and 1153 to 897 cm<sup>-1</sup> is observed. This consequently induced an increment in the intensity peaks of 1750 cm<sup>-1</sup> (C=O groups), 1705 cm<sup>-1</sup> (COOH groups) and 1634 cm<sup>-1</sup> (C=N-).

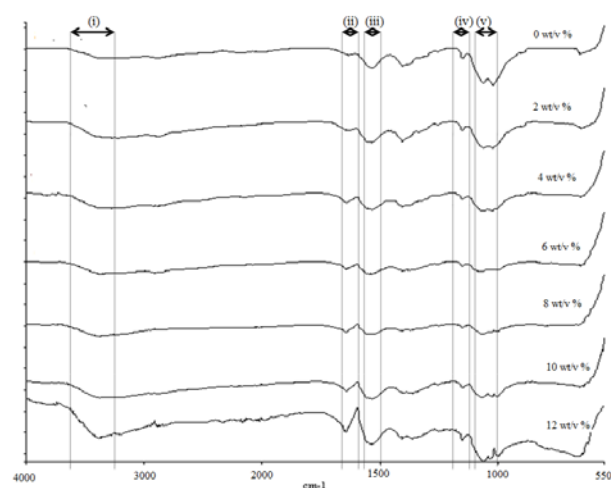


FIG. 8 THE FTIR SPECTRUM OF THE BIO-COMPOSITES; (A) 0ODAC (B) 2ODAC (C) 4ODAC (D) 6ODAC (E) 8ODAC (F) 10ODAC (G) 12ODAC AT DIFFERENCE RESPECTIVE WAVELENGTH (I) 3500-3400 CM<sup>-1</sup> (II) 1670-1600 CM<sup>-1</sup> (III) 1550-1500 CM<sup>-1</sup> (IV) 1310-1200 CM<sup>-1</sup> AND (V) 1110-890 CM<sup>-1</sup>

The inter H bonds between Cs and ODAC molecules assigned by 3100 to 3600cm<sup>-1</sup> (OH stretching), 3520 to 3400 cm<sup>-1</sup> (NH<sub>2</sub>) and 1725 to 1700 cm<sup>-1</sup> (COOH) peaks. The intensity of these peaks is broadened and lowered to almost 12 to 14 cm<sup>-1</sup> with the addition of ODAC filler. Thus, more H bonds obtained from the bio-composites with greater content of ODAC filler.

The electrostatic interactions of Cs and ODAC molecules assigned by an increment in intensity of 2500 cm<sup>-1</sup> (asymmetric NH<sub>3</sub><sup>+</sup> cations), 1548 to 1560 cm<sup>-1</sup> peak (symmetric NH<sub>3</sub><sup>+</sup> cations), 1450 cm<sup>-1</sup> (asymmetric COO<sup>-</sup> ions) and 1408 cm<sup>-1</sup> (symmetric COO<sup>-</sup> anions) peaks. Simultaneously, the reduction of 3520 to 3400 (NH<sub>2</sub>), 1735 cm<sup>-1</sup> (COOH) and 1650 cm<sup>-1</sup> (C=O and N-H) peaks are observed. Both phenomenons are significantly occurred for the bio-composites with more ODAC fillers.

### FTIR analysis of swollen bio-composites in acidic media

The FTIR spectrum of the swollen bio-composites in acidic media is illustrated in Fig. 9a and b. The spectrum of the swollen bio-composites in higher pH (pH 6) shows a wider NH region (3520 to 3400 cm<sup>-1</sup>), indicates the unbounded NH<sub>2</sub> groups. At the higher pH medium lesser amount of H<sup>+</sup> ions present for the protonization of NH<sub>2</sub> groups (Fig. 9a). The alteration in intensity of 2500 cm<sup>-1</sup>(NH<sub>3</sub><sup>+</sup>), 1630 (NH-R) and 1512 cm<sup>-1</sup> (NH<sub>2</sub>) peaks confirmed the protonization process of the swollen bio-composites.

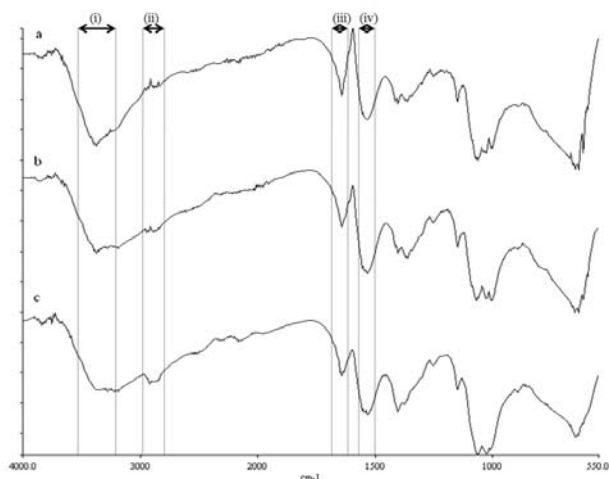


FIG. 9 a THE FTIR SPECTRUM OF 8ODAC BIO-COMPOSITES IN; (A) PH2 (B) PH4 AND (C) PH 6 AT DIFFERENCE RESPECTIVE WAVELENGTH (I)3520-3400 CM<sup>-1</sup> (II) 2500 CM<sup>-1</sup> (III) 1630 CM<sup>-1</sup> AND (IV) 1512 CM<sup>-1</sup>

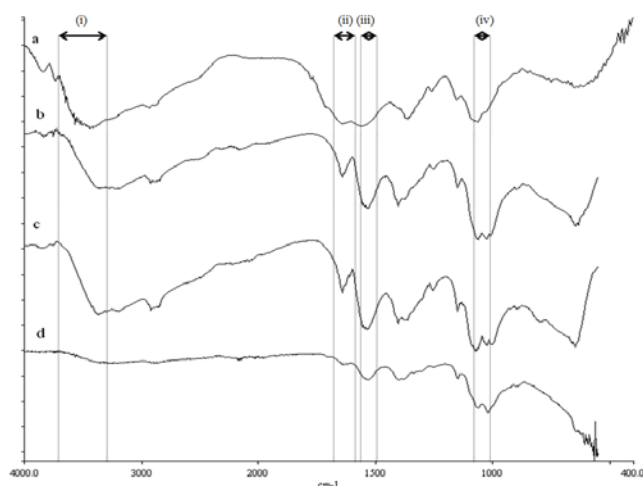


FIG. 9 b THE FTIR SPECTRUM OF THE BIO-COMPOSITES IN PH 4; (A) 0ODAC (B) 4ODAC (C) 8ODAC AND (D) 12ODAC AT DIFFERENCE RESPECTIVE WAVELENGTH (I) 3450-2800 CM<sup>-1</sup> (II) 1722-1632 CM<sup>-1</sup> (III) 1582-1533 CM<sup>-1</sup> (IV) 1032-1039 CM<sup>-1</sup>

The following peaks; 3080 cm<sup>-1</sup> (NH-R groups of ODAC filler), 2965 cm<sup>-1</sup> (CH<sub>3</sub>), 2925 cm<sup>-1</sup> (CH<sub>2</sub>), 2876 cm<sup>-1</sup> (CH) and 900 cm<sup>-1</sup> (glycosidic linkage) are consistently presents in the swollen bio-composites. These peaks proved, the molecular frame of the bio-composites is maintained with no scissoring of the polymer chains during the swelling process.

Fig.9b illustrated the FTIR spectra of the swollen bio-composites in acidic media with different ODAC filler content. The protonization of NH<sub>2</sub> groups assigned a wider and smooth spectra of 3450 to 2800 cm<sup>-1</sup> (NH<sub>2</sub>) and presences two new peaks; 1630 cm<sup>-1</sup> (asymmetric NH<sub>3</sub><sup>+</sup>) and 1533 cm<sup>-1</sup> (symmetric NH<sub>3</sub><sup>+</sup>). The adsorption peaks of C-OH and COO<sup>-</sup> groups are blue-shifted from

1032 to 1039 cm<sup>-1</sup> and 1582 to 1586 cm<sup>-1</sup>; results in dissociation of COOH groups of ODAC filler. The dissociation also brought in the reduction of 1624 cm<sup>-1</sup> (COOH) peaks. Furthermore, the 1679 cm<sup>-1</sup> peak is shifted by 43 cm<sup>-1</sup> as compared to the original intensity of 1722 cm<sup>-1</sup> (C=O bands) peaks. The above phenomenon is brought by the interaction of H<sup>+</sup> ions with the C=O groups of ODAC filler.

#### FTIR analysis of swollen bio-composites in neutral media

Fig. 10 illustrated the FTIR spectrum of the swollen bio-composites in neutral media. The interactions of H<sub>2</sub>O molecules with the bio-composites involved 3450 to 3400 (OH and NH<sub>2</sub>), 1550 and 1690 cm<sup>-1</sup> (NH-R), 1651 cm<sup>-1</sup> (C=O of the NH-R) and 1585 to 1420 cm<sup>-1</sup> (symmetric and asymmetric COOH) peaks. The interactions slightly shift the above peaks to the lower intensity and wave length. There is also a significant shift on the NH-R band from 1660 cm<sup>-1</sup> for the non swollen to 1640 cm<sup>-1</sup> for the swollen bio-composites.

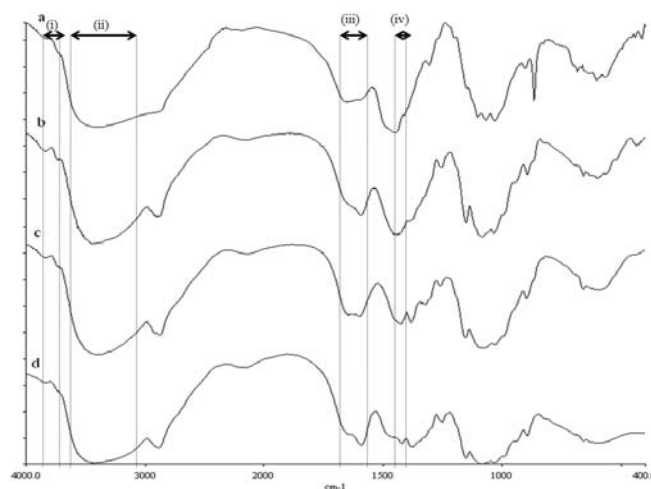


FIG. 10 THE FTIR SPECTRUM OF THE BIO-COMPOSITES IN PH 7; (A) 0ODAC (B) 4ODAC (C) 8ODAC AND (D) 12ODAC AT DIFFERENCE RESPECTIVE WAVELENGTH (I) 3756-3617 CM<sup>-1</sup> (II) 3459-3400 CM<sup>-1</sup> (III) 1595-1589 CM<sup>-1</sup> (IV) 1420 CM<sup>-1</sup>

#### FTIR analysis of swollen the bio-composites in alkaline media

Fig. 11 illustrated the FTIR spectrum of the swollen bio-composites in alkaline media. Generally, the FTIR spectrum of the bio-composites is insignificantly influenced by the swelling process.

The peaks of 3440 cm<sup>-1</sup> (OH and NH<sub>2</sub>), 2910 cm<sup>-1</sup> (C-H), 1653 cm<sup>-1</sup> (C=O), 1580 cm<sup>-1</sup> (deformation of the N-H bonds of NH<sub>2</sub> groups), 1417 cm<sup>-1</sup> and 1377 cm<sup>-1</sup>

(coupling of C-N axial stretching and N-H angular deformation) and 1153 to 897  $\text{cm}^{-1}$  (C-O-C of glycosidic linkage) is constantly appeared for all swollen bio-composites (Fig. 11).

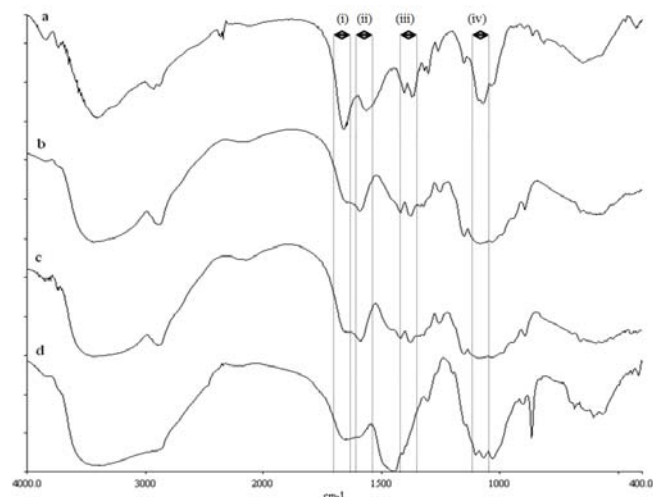


FIG. 11 THE FTIR SPECTRUM OF THE BIO-COMPOSITES IN PH 8; (A) 0ODAC (B) 4ODAC (C) 8ODAC AND (D) 12ODAC AT DIFFERENCE RESPECTIVE WAVELENGTH (I) 1655-1638  $\text{CM}^{-1}$  (II) 1400  $\text{CM}^{-1}$  (III) 1153  $\text{CM}^{-1}$  (IV) 897  $\text{CM}^{-1}$

## Conclusions

The hydrophilicity of Cs film was reduced with addition of 0 to 12 wt/v % of ODAC filler. The addition increased the rigidity and compatibility and consequently reduces the swelling profile of the bio-composites. The results were attributed to:

- The good compatibility of Cs matrix and ODAC filler; derived from the formation of the electrostatic interactions and inter hydrogen bonds at the interfacial region.
- Chemical properties of the bio-composites; brought by the protonization, dissociation, hydrophilic, hydrophobicity and configuration of the  $\text{NH}_2$ ,  $\text{NH-R}$ ,  $\text{C=O}$ ,  $\text{COOH}$ , benzene ring.
- Physical properties of the bio-composites; brought by the thickness, cross linked structured and compactly of the bio-composites.

FTIR analysis was applied to understand and proved the effects of the mentioned factors on the swelling properties of the composites film. Lastly, the bio-composites have natural resistance properties in various pH media and find in various engineering applications.

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